SCIENCE FOR GLASS PRODUCTION

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SOL-GEL COATINGS ON FLOAT GLASS

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The refractive coefficients and thickness of two-sided sol-gel coatings of different compositions deposited on float glass by the immersion method are measured. It is established that the refractive coefficient on the top surface of a sample, which contacts the protective atmosphere of the melt tank during glass working, is higher and the film thickness is smaller than those on the bottom surface. This is due to the different properties of the opposite surfaces of thermally polished glass, which is related to the different tin concentrations in the surface layers.

The traditional method for producing glass with a set of required service properties is based on correcting the glass composition by introducing additional components. This requires substantial expenses and drastic changes in machinery and production technology. A cheaper and more advanced way is modifying the surface glass layer by applying thin coatings. This method has long been used extensively in the production of optical instruments for the purpose of "clarifying" (increasing the transmission coefficient) of glass parts. For this purpose a silicon dioxide film is deposited on glass surface, since its refractive index is lower than that of the glass part material.

A wide range of architectural and building sheet glasses is currently produced by modifying the surface of clear float glass using polymeric, oxide, oxide-metallic, or other functional films.

Sol-gel technology is one of the variants for chemical application of coatings. In this technology a film-forming solution (FFS) containing all the needed oxides together with a low-boiling solvent is applied to one or two opposite surfaces of glass heated to about 400°C or to cold glass. In the latter case the film is fixed by short-term firing at a low temperature. Sol-gel technologies offer a wide product range; antiflash, light-shielding, decorative, conducting, heat-reflecting, hardened glasses, etc. (U.S. patent No. 6472012, France patent application No. 2827855) [1, 2].

The service parameters of glass produced by sol-gel technology to a large extent depend on the type of materials used for film-forming oxides [3], the time-temperature conditions of preparation, maturing, and application of FFS [4, 5], etc. Experience shows that when float glass is used as a substrate, the thickness, refractive coefficient, and spreadability of sol-gel coatings on the opposite surfaces differ to a certain extent, which may be related to the different properties of the two sides.

Indeed [6], the concentration of tin in the surface adjacent to the tin melt (the bottom surface) and the one contacting the float-tank atmosphere (the top surface) decreases from the surface into the glass layer to a depth of 20 – 30 μm. The tin content on the top side is regularly lower (around 0.1% in the surface layer) than on the bottom side (approximately 2%) [7]. Tin is present in the surface layers [6] mainly in the form of Sn^{2+} and in the deeper layers in the form of Sn^{4+}; moreover, the reduced tin concentration is significantly lower on the glass side contacting the protective atmosphere.

The concentration of tin leads to structural modifications: a decreased number of bridge Si – O – Si bonds and an increased number of nonbridge $Si – O^-$ bonds [7]. Since the tin content on the upper and lower surfaces differs by about an order of magnitude, not only the composition but also the degrees of structural modifications on the opposite sides differ [7]. This leads to a difference in their properties, in particular, the refractive index on the bottom surface is larger by about three units of the third decimal place than on the top surface. There is also a regular insignificant difference in the light reflection coefficients. The lower surface has a larger wetting angle than the top surface.

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TABLE 1

Sample	Refractive coefficient		Mirror reflection coefficient, %		Film thickness, Å	
	top side	bottom side	top side	bottom side	top side	bottom side
1	1.813	1.790	17.6	17.3	350	390
2	2.085	2.061	37.1	36.8	280	350

The present study investigates the effect of the float glass surface on the refraction coefficient and the thickness of multicomponent oxide sol-gel coatings.

Samples of size 70 × 70 × 4 mm were cut out from the same glass sheet to minimize the effect of the variations in tin concentration in the surface layer in the industrial production of float glass. Bilateral sol-gel coatings of different compositions were applied to these samples by immersion and fixed by firing at 450°C for 30 min.

The refractive index n and the film thickness were determined with an LÉF 3-M1 ellipsometer for the glass surface contacting the protective tank atmosphere in the glass ribbon production (the top side) and that contacting the tin melt (the bottom side). The mirror reflection coefficient was measured with a Pulsar instrument in the wavelength interval of 380 – 720 nm.

The main service property of a "cold window," which protects interiors from excessive illumination and overheating in summer period, is a high mirror reflection coefficient. The higher the refractive index of the functional film, which depends on the FFS composition and its application conditions, and the lower this index in the substrate glass, the higher the mirror reflection coefficient. The refractive index of the substrate depends on its composition and for float glass it additionally depends on the concentration of tin in the surface layer.

As important property is spreadability, i.e., the ability of a FFS to spread uniformly over the surface and to form a coating without discontinuities and inhomogeneities. To achieve this, the film-forming solution should not tend to form heterogeneities and the glass ought to be well wettable by the solution, which depends on the contact wetting angle.

Table 1 compares the refractive coefficient, thickness, and mean mirror reflection coefficient R (in the wavelength interval of 380 – 720 nm) for float glass with sol-gel coatings of two different compositions.

It is known that when light passes from a less dense medium to an optically denser medium, the refractive index is larger than unity, and in the opposite case, the refractive index is below unity [8]. In the considered cases light passes from the same medium (the film) to the media with different refractive indexes and optical densities (the top and the bottom of the substrate). Since the values n on the bottom side are slightly larger, it can be expected that the functional film on this optically denser side of float glass has a lower refractive index. Indeed (Table 1), the parameter n of the films on the bottom side of the samples is approximately 1% lower than on the opposite side. The same regularity is also observed for R, which is proportionally related to the refractive index according to the following formula [9]:

$$R = \left(\frac{n-1}{n+1}\right)^2.$$

It can be seen from the data in Table 1 that the film on the bottom surface of glass is 5 – 11% thicker than on the opposite side. This can be attributed to the different contact wetting angles of the glass surface containing tin and glass without tin; for water this difference reaches 20° or more [7].

To verify the reliability of the described regularities that correlate the physical characteristics of sol-gel films to the type of the substrate surface, we have measured the refractive index and thickness of 20 coatings of different compositions. It was found that in 85% of samples the refractive coefficient is higher on the upper side than on the lower side. Vice versa, the film thickness on the bottom side is smaller than on the top side in 80% samples. This agrees with the conclusions derived from the data in Table 1.

The relative difference Δ between the measured values of the refractive index and the thickness of sol-gel films applied to both sides of float glass is calculated from the expression

$$\Delta = \frac{\text{max - min}}{\text{max}} \times 100\%,$$

where max and min are, respectively, the larger and the smaller values of the refractive coefficient (thickness) of a particular film.

Thus, the relative difference in the refractive coefficient measured on two sides was equal to (%): up to 0.5 (in 3 films, or 15% of films considered); 0.5 – 1.0 (4 films, or 20%); 1.0 – 2.0 (8 films, or 40%), from more than 2.0 to 3.0 (5 films, or 25%). The relative difference in the film thickness determined on both sides was equal to (%): up to 5 (5 films, or 25%), 5 – 10 (4 films, or 20%), 10 – 20 (7 films, or 35%), over 20 (4 films or 20% of films considered). It was found that the refractive coefficients of the films on different sides of the substrate differ only by 0.3 – 3.0%, whereas the difference in thickness is more significant and may reach 35%.

Thus, when a sol-gel coating is deposited on both sides of a float-glass sheet by the immersion method, its refractive index on the top side of the sample is larger and the thickness of the coating is smaller than on the bottom side.

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